

trolled caustic fusion,⁷ oxidation with silver oxide,^{8,9} mercuric oxide,¹⁰ and gold oxide¹⁰ and by the Cannizzaro reaction of vanillin in the presence of a silver catalyst.¹¹ Vanillic acid has been prepared indirectly from vanillin by the hydrolysis of acetylvanillic acid prepared by oxidation with peracetic acid of acetylvanillin,¹² and by the hydrolysis of acetovanillonitrile prepared by the reaction of vanillin oxime with acetic anhydride.¹³ The procedures described are essentially those reported by Pearl.^{7,8}

¹ Tiemann, *Ber.*, 8, 1134 (1875).

² Ciamician and Silber, *Ber.*, 38, 3821 (1905).

³ Robbins and Lathrop, *Soil Sci.*, 7, 475 (1919).

⁴ Dorland and Hibbert, *Can. J. Research*, 18B, 33 (1940).

⁵ Lock, *Ber.*, 62, 1187 (1929).

⁶ Sabalitschka and Tietz, *Arch. Pharm.*, 269, 545 (1931).

⁷ Pearl, *J. Am. Chem. Soc.*, 68, 2180 (1946).

⁸ Pearl, *J. Am. Chem. Soc.*, 68, 429 (1946).

⁹ Pearl, *J. Am. Chem. Soc.*, 68, 1100 (1946).

¹⁰ Pearl, *J. Am. Chem. Soc.*, 67, 1628 (1945).

¹¹ Pearl, *J. Org. Chem.*, 12, 79 (1947).

¹² Böeseken and Greup, *Rec. trav. chim.*, 58, 528 (1939).

¹³ Raiford and Potter, *J. Am. Chem. Soc.*, 55, 1682 (1933).

VINYL LAURATE AND OTHER VINYL ESTERS

(Lauric acid, vinyl ester)



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1. Procedure

In a 500-ml. round-bottomed three-necked flask provided with a thermometer, a reflux condenser, and a gas inlet tube through which a stream of nitrogen is passed (Note 1) are placed 206 g. (2.4 moles) of freshly distilled vinyl acetate (Note 2) and 80 g. (0.4 mole) of lauric acid (Note 3). The lauric acid is dissolved by

warming, and 1.6 g. of mercuric acetate is added. The mixture is shaken by hand for about 30 minutes, and 0.15 ml. of 100% sulfuric acid is added dropwise (Note 4). The solution is heated under reflux for 3 hours, then 0.83 g. of sodium acetate trihydrate is added to neutralize the sulfuric acid. The excess vinyl acetate is recovered by distillation at atmospheric pressure (vapor temperature about 70–80°) until the pot temperature reaches 125° (Note 5). The distillation is completed at 10 mm. or lower (Note 5), and, after the collection of a small quantity of low-boiling material, fairly pure vinyl laurate (Note 6) is obtained as a colorless liquid, b.p. 142–143°/10 mm. (138–139°/8 mm.; 124–126°/3 mm.). The yield is 50–57 g. (55–63%). Redistillation (Note 7) yields 48–53 g. (53–59%) of pure vinyl laurate, b.p. 142–142.5°/10 mm. (120–120.5°/2 mm.); n_D^{25} 1.4387 (Notes 8 and 9).

2. Notes

1. All operations should be conducted in a nitrogen atmosphere to minimize the formation of polymer.

2. An Eastman Kodak Company practical grade of vinyl acetate is satisfactory. It was distilled immediately before use through a 48 by $\frac{3}{4}$ in. column packed with $\frac{3}{32}$ -in. single-turn Pyrex glass helices. The checkers employed material obtained from the Niacet Chemicals Division, Niagara Falls, New York, distilled once through a 12-in. Vigreux column, b.p. 73°/746 mm.

3. Lauric acid, m.p. 44°, was prepared from the commercial acid obtained from Armour and Company, Chicago, Illinois. The acid was recrystallized twice from acetone at –40° (10 ml. of acetone per gram of acid) and distilled under reduced pressure through a well-insulated, electrically heated 30 by 1 in. column packed with $\frac{1}{4}$ -in. Berl saddles. Pure lauric acid has a boiling point of 167–168°/8 mm. and n_D^{45} 1.4316. The Eastman Kodak Company grade of lauric acid melting at 43–44° is satisfactory.

4. The 100% sulfuric acid is prepared by cautiously adding 7.3 g. of fuming sulfuric acid containing 30% sulfur trioxide to 10 g. of 95% sulfuric acid.

5. An electrically heated 18 by 1/2 in. Vigreux column was employed.

6. The vinyl laurate, which has an acid number of about 2, usually contains a small quantity of mercury at this stage, from which it can be separated by decantation.

7. Sufficient sodium bicarbonate is added to the pot charge to neutralize the free acid present (see Note 6).

8. Additional properties of vinyl laurate are n_D^{35} 1.4345 and d_4^{30} 0.8639. If the iodine number is determined by the Wijs method, a 200% excess of iodine chloride solution and a 1-hour reaction period should be employed in order to obtain values which are 97-99% of the theoretical value.

9. Vinyl caproate, caprylate, pelargonate, caprate, myristate, palmitate, stearate, 10-hendecenoate (undecylenate) and oleate can be prepared in a similar manner, except that in the preparation of the palmitate and stearate the fatty acids are added to a solution of mercuric acetate and sulfuric acid in vinyl acetate. Vinyl stearate is not redistilled, but the once-distilled product is recrystallized from acetone at 0° (3 ml. of acetone per gram of vinyl stearate). The amount of mercuric acetate employed was 2%, and the amount of 100% sulfuric acid was 0.3-0.4%, of the weight of the stearic acid. Average yields and properties of these vinyl esters are given in the table.

VINYL ESTER	YIELD, %	BOILING POINT		n_D^{30}	d_4^{30}
		°C.	mm.		
Caproate	40	98-99	100	1.4159	0.8837
Caprylate	55	134-135	100	1.4256	0.8719
Pelargonate	55	133-133.5	50	1.4291	0.8689
Caprate	45	148	50	1.4320	0.8670
Myristate	60	147-148	4.8	1.4407	0.8617
Palmitate (m.p. 26.7-27.1°)	35	168-169	4.5	1.4438	0.8602
Stearate (m.p. 35-36°)	30	187-188	4.3	1.4423 (at 40°)	0.8517 (at 40°)
10-Hendecenoate	70	124-124.5	10	1.4442	0.8799
Oleate	60	178	2.8	1.4533	0.8691

The acids used for preparing the vinyl esters tabulated were Eastman Kodak Company pure grade except for the following,

which were obtained from the companies indicated and purified by fractionation through an efficient fractionating column: caproic acid, b.p. 96°/8 mm., Carbide and Carbon Chemicals Corporation, New York; caprylic acid, b.p. 124–125°/8 mm., capric acid, b.p. 145–146°/8 mm., Armour and Company, Chicago, Illinois; pelargonic acid, b.p. 176°/64 mm., Emery Industries, Cincinnati, Ohio; 10-hendecenoic (undecylenic) acid, b.p. 177–180°/25 mm., Baker Castor Oil Company, New York. Oleic acid was prepared from olive-oil fatty acids by low-temperature crystallization and distillation.¹

3. Methods of Preparation

The procedure described is substantially that of Toussaint and MacDowell,² with minor modifications.³ Vinyl esters of long-chain aliphatic acids have also been prepared by the reaction of acetylene with the appropriate acids,^{4,5,6} but this reaction is not so convenient for small-scale laboratory preparations.

¹ Brown and Shinowara, *J. Am. Chem. Soc.*, **59**, 6 (1937); Wheeler and Riemschneider, *Oil and Soap*, **16**, 207 (1939).

² Toussaint and MacDowell, U. S. pat. 2,299,862 [*C. A.*, **37**, 1722 (1943)].

³ Swern, Billen, and Knight, *J. Am. Chem. Soc.*, **69**, 2439 (1947); Swern and Jordan, *J. Am. Chem. Soc.*, **70**, 2334 (1948).

⁴ Reppe, Ger. pat. 588,352 [*C. A.*, **28**, 1357 (1934)]; U. S. pat. 2,066,075 [*C. A.*, **31**, 1037 (1937)].

⁵ Imperial Chemical Industries, Brit. pat. 581,501 [*C. A.*, **41**, 2428 (1947)].

⁶ Powers, *Ind. Eng. Chem.*, **38**, 837 (1946).